

**INVESTIGATIONS
OF INNER ELECTRON SHELLS
BY SPECTROSCOPIC STUDIES
OF PHOTO- AND AUGER
ELECTRONS**

By

EVELYN SOKOLOWSKI

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ALMQVIST & WIKSELLS BOKTRYCKERI AB

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INAUGURAL DISSERTATION

by

EVELYN SOKOLOWSKI

FIL. LIC., STHLM

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To my Parents

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SUMMARY

When the fundamental properties of the atom were explored early in this century the development was guided mainly by the results of the optical and X-ray spectroscopist. Eventually quantum mechanics could be brought into good quantitative accordance with the X-ray spectroscopic observations of the most simple atomic systems. For the more complex ones, an exact theoretical treatment became too unwieldy, although in principle the existing theories were expected to account completely for all the phenomena observed. At this stage precision X-ray spectroscopy of the heavier elements and of solids seemed doomed to remain an empirical science, which led to a certain stagnation of this field of research, particularly since at the same time nuclear physics began to divert the attention of the physicists.

However, the interest in atomic physics was revived as technology began to demand a wider knowledge about the structure and properties of solids. Although exact theoretical formulations were still unpracticable in many cases, it was found that simple semi-empirical models often gave surprisingly good results. Also, the development of electronic calculating machines brought within reach solutions that had seemed unattainable a few decades earlier. The results of X-ray spectroscopy were now reconsidered and full use was often made of the precision of the experimental data. At this point it was to be regretted that the data pertaining to inner electron levels were all obtained by rather similar methods and that therefore systematic errors could not be precluded.

In the present papers the K and L electron levels in a series of solids have been studied by a method differing fundamentally from those used in conventional X-ray spectroscopy. Electrons from the inner atomic shells are expelled by X-radiation of given energy and the electron momenta are analyzed with a magnetic spectrometer of high precision. It can be shown that by this method the final state of the expelled electron is well defined.

Paper I describes the experimental arrangements as well as some preliminary measurements. It is shown that the lines observed in the electron spectra have their origin in two different processes: the photo effect and the Auger effect. The spectrum of metallic Cu is analyzed and preliminary values for the K and L_I binding energies as well as for the KLL and KLM Auger energies are given. The errors pertaining to different calibration methods are discussed.

An extensive theoretical treatment of KLL and KLM Auger spectra has recently

been given by Aasad and Burhop, exemplifying the renewed interest in the theoretical problems of atomic physics. In *paper II* the *KLL* Auger groups of Cu and Ge are studied experimentally. Good agreement is found between experiment and theory regarding the relative energies and intensities of the lines, which confirms the assumptions of "intermediate coupling" for the fourth period elements. The absolute energies of the *KLL* Auger groups are found to deviate considerably from the calculated values.

In *paper III* the *K* and *L* shells of copper are studied in the case of the pure metal and the cuprous and cupric oxides. In all cases a shift is observed towards greater binding energy in the oxide, this shift being greatest for the *1s* and *2s* levels in the cupric oxide. The observed shift in the *K* binding energy for CuO is correlated to investigations on the band structure of the oxide. Indications are found of changes in the natural line widths in connection with oxidation. A line in the *KLL* Auger spectrum from metallic copper is compared with the corresponding line from CuO. The line from the oxide is found to be somewhat lower in energy. Also, there is some evidence that the *K* Auger yield depends on the chemical composition of the source.

In *paper IV* some instrument corrections, necessary at low energies for a precision of the order $1:10^5$, are introduced. The energies obtained by the present method are correlated to the usual X-ray spectroscopic definition of binding energy. The photo electron method is applied to a systematic study of *K* binding energies in the fourth and *L* binding energies in the sixth period of the periodic table. For the *L* energies the precision achieved is one order of magnitude higher than that attained by conventional X-ray methods. In the case of the *K* energies marked deviations from X-ray data are observed in some instances. These are discussed in terms of the band structure of metals. The use of infinitely thick sources in precision spectroscopy is demonstrated.

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When the iron-free double-focussing spectrometer of this institute was designed, Professor Kai Siegbahn had already recognized and bore in mind the desirability of studying electron binding energies by a method alternative to the conventional X-ray procedures. After having initiated this work Professor Siegbahn maintained a never-failing interest, which often manifested itself in concrete suggestions and provided a most valuable source of encouragement and stimulation. It is therefore a great pleasure for me to acknowledge my gratitude to Professor Siegbahn.

Most of the methods and data presented in this work are results of my collaboration with Fil. lic. Carl Nordling, to whom I wish to express my sincere thanks.

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EVELYN SOKOLOWSKI

